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SILICATE ENERGY: A MYTH OR REALITY?

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The proposals of A. I. Kulikov on developing power plants using high-modulus silicates as a fuel published in the scientific literature are discussed. Based on thermodynamic estimates, the conclusion about the impossibility of creating such plants is substantiated.

The decrease in available power resources motivates the growing interest in new alternative types of fuel, especially high-calorie and environmentally safe fuel applicable to vehicle engines. Oil and gas reserves are limited. Coal cannot yet compete with oil as a source of liquid fuel. The use of coal in electric power plants involves the necessity of taking measures to protect the ambient air from toxic emission and utilize the waste ash. Nuclear power, in spite of its advantages, is a serious concern in society. All this promotes interest, sometimes of a sensational nature, in new ideas and proposals in this sphere.

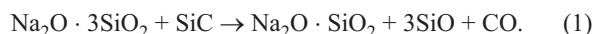
Authors proposing new ideas often concentrate on the prospects to consumers and gloss over possible problems. Silicate energy is precisely an idea of this kind [1]. Its author A. I. Kulikov promotes his views in popular magazines and specialized journals, mostly stressing the advantages involved in the prospect of using the new fuel proposed by him and neglecting the details of the process. He benefits from ignorance of the nuances of the physical chemistry of silicates on the part of the potential users of his idea. Since there is a constantly growing demand in alternative new kinds of fuel, corresponding offers are bound to arise.

A. I. Kulikov proposes using high-modulus sodium or potassium silicates as fuel: $\text{Na}_2\text{O} \cdot m\text{SiO}_2$ and $\text{K}_2\text{O} \cdot m\text{SiO}_2$, where m is the silica modulus. The silica modulus (the $\text{SiO}_2 : \text{M}_2\text{O}$ molar ratio, where M is Na or K) in liquid glasses is equal to 2.6–3.5. A. I. Kulikov proposes using silicates with a modulus equal to 3 for sodium and equal to 4 for potassium [2]. The higher the silica modulus, the easier the liquid glass disintegrates in air with the formation of amorphous SiO_2 [3]. The main reason is the replacement

(displacement) of the silicic acid anion by the anion of the stronger carbonic acid formed as a result of the presence of carbon dioxide in air.

A. I. Kulikov proposes using the decomposition of high-modulus silicates under the effect of oxygen-free siliceous compounds, in particular silicon carbide SiC [1]. He argues that the reaction of decomposition of high-modulus silicates proceeds according to the chain mechanism. He proposes using silicon carbide in the form of rods introduced into the reaction zone to control it, similarly to a nuclear reactor. He suggests using SiC rods instead of boron rods in engines proposed by him.

A. I. Kulikov in [2] asserts that a high-modulus silicate disintegrates in the presence of silicon carbide with the silica modulus decreasing from 3 to 1:



However, this reaction is endothermic, which requires large energy consumption, and no energy is released. The thermal effect of this reaction can be estimated based on the Hess' law using the reference data from [3–5]. For reaction (1) $\Delta H_{\text{th}}^0 = +1511.17$ kJ/mole, i.e., this is a highly endothermic reaction. According to the data in [6], it was calculated for $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ that $C_r^0 = 233.13$ J/(mole · K). For reaction (1) $\Delta C_r^0 = -29.24$ J/(mole · K), which shows that its endothermic effect decreases with increasing temperature [7]. However, even if the reaction at a high temperature becomes exothermic, its thermal effect cannot be substantial and some energy is needed to heat the initial mixture.

A. I. Kulikov maintains that high-modulus silicates have a high lattice energy, which is 4 times higher than the heat generated in fuel oil combustion [1], but neglects the fact that the crystal lattice energy is only partly transformed into heat

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and the rest is accumulated as the energy of the chemical bonds of the reaction products (in this case, low-modulus silicates and silicon and carbon oxides).

Let us write the reaction of disintegration of high-modulus silicates as follows:



For this reaction $\Delta H_{\text{th}}^0 = +47$ kJ/mole, i.e., at room temperature it proceeds consuming heat. For reaction (2) $\Delta C_r^0 = -33.35$ J/(mole · K), which shows that its endothermic effect decreases with increasing temperature [7]. However, even if this reaction at a high temperature becomes exothermic, some energy is required to heat the initial material.

From the possibility of spontaneous disintegration of high-modulus silicates in air, A. I. Kulikov draws an unjustified inference that SiC acts as the initiator of a chain reaction of decomposition of high-modulus silicates. Apparently, the reason for the publication of his paper in such a serious scientific journal is the fact that the chemical reaction of disintegration of high-modulus silicates and the type of the chain reaction are formally correctly written in this paper. However, neither this paper nor the others offer any proofs of the fact that the described reaction of disintegration of high-modulus silicates proceeds in accordance with the written equations, especially in accordance with the chain mechanism.

When a high-modulus silicate reacts with silicon carbide, heat may be generated due to the oxidation of carbide, since the high-modulus sodium silicate is already maximally oxidized and can be reduced by absorption of energy from the ambient environment:



For reaction (3) $\Delta H_{\text{th}}^0 = -138.63$ kJ/mole, and for reaction (4) $\Delta H_{\text{th}}^0 = -1123$ kJ/mole (reference data from [3, 5]). For reaction (3) $\Delta C_r^0 = +2.87$ J/(mole · K), i.e., with increasing temperature, the thermal effect will decrease. For reaction (4) $\Delta C_r^0 = -7$ J/(mole · K), i.e., the thermal effect will grow with increasing temperature. The formation of CO_2 facilitates the disintegration of the high-modulus silicate, which also contributes to a certain release of heat:



The thermal effect of this reaction $\Delta H_{\text{th}}^0 = -55.09$ kJ/mole (reference data from [3–5]). For reaction (5) $\Delta C_r^0 = -23.46$ J/(mole · K), which points to an increasing thermal effect as the temperature increases [7].

The experience of using silicon carbide heaters indicates that silicon dioxide emerging as the reaction product forms a layer on the SiC surface, which effectively prevents further

oxidation. The presence of alkaline metal oxides perceptibly accelerates the oxidation of SiC. This is confirmed by the accelerated oxidation of silicon carbide heaters in furnaces with an increased concentration of alkaline metal oxides in the gaseous phase. Heating of a mixture of silicon carbide powder with liquid glass in a furnace does not lead to a chain reaction (explosion). The process is soon retarded by the reaction products localized on the surface of the SiC particles. It should be noted that this does not exclude the possibility of silicon carbide oxidation proceeding in accordance with the chain mechanism. Such reaction can probably take place in the conditions of a shock-wave impact (in the conditions of an explosion), but this is a totally different application area.

There are no prospected natural deposits of high-modulus silicates and silicon carbide (or silicon nitride) on Earth. This at once puts them at a disadvantage compared with oil, gas, and coal. Artificial synthesis of high-modulus silicates and especially of silicon carbide requires a substantial consumption of energy that has to be procured using other kinds of fuel. For instance, liquid glass at present is obtained by melting SiO_2 with soda or soda with sodium sulfate in glass-melting tank furnaces heated by natural gas [3]. The synthesis of silicon carbide from silicon dioxide and carbon using the Acheson method is performed in electric arc furnaces at temperatures of 1600–2800°C [3]. The processes of synthesis both of high-modulus silicate and of silicon carbide are accompanied by energy losses in the form of heat emissions into the ambient medium. This presents difficulties when attempting to use these materials for energy accumulation. When the accumulated energy is released from the synthesized compounds, energy losses cannot be avoided either. Thus, the absence of natural deposits of silicon carbide or nitride makes their use as a fuel alternative to oil, coal, and gas problematic. The synthesis of silicon carbide and high-modulus silicates requires substantial energy consumption and is accompanied by energy losses.

Let us analyze some engineering problems related to the use of silicon carbide or nitride as fuel. In combustion they release silicon dioxide, which is an abrasive material. This will cause increased wear of engine parts and contaminate the channels removing the combustion products. Even if one develops conditions for the formation of volatile silicon monoxide inside the combustion chamber, it has to somewhere transform into a solid phase, which will contaminate the channels for the outlet of the combustion products. Moreover, the formation of SiO instead of SiO_2 decreases the thermal effect of the reaction of SiC oxidation. The silicon oxide or dioxide powder released from the engine will entrain a lot of heat and decrease the useful work.

The released powder will be highly dispersed, which represents a danger to the environment and to human health. It is known that the aspiration of highly-disperse silicon dioxide particles may cause a disease known as silicosis. If one could develop a vehicle operating silicon carbide or nitride, in a certain while a layer of silicon oxide powder would be

formed on the sides of the road. It would be very difficult to entrap and carry away or periodically dump this powder.

The engine described in [1] is a typical "perpetual motion" engine, and although A. I. Kulikov insists that this is not so, it does not prove anything. Energy already has been consumed and accumulated in this process during the synthesis of high-modulus silicate and silicon carbide. Energy will be irrevocably spent on the useful work and losses, and the recovery of the products to restore the silicon carbide rods cannot compensate for this consumption.

Summing up, it should be noted that heat release in the decomposition of high-modulus sodium or potassium silicates in the presence of silicon carbide is possible not according to the mechanism proposed by A. I. Kulikov but in the course of oxidation of silicon carbide by air oxygen. Natural deposits of silicon carbide and nitride and of high-modulus alkaline metal silicates on Earth are absent and their artificial synthesis requires substantial energy consumption with the corresponding energy losses. In other words, the considered process cannot be a source of energy and can be only a consumer of energy, for instance, in creating energy reserves. An attempt to use these materials as fuel will create

big engineering and environmental problems related to the emission of highly disperse hot powder of silicon dioxide or monoxide.

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